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# State-to-State Kinetics and Transport Properties of Electronically Excited N and O Atoms

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**Abstract.** A theoretical model of transport properties in electronically excited atomic gases in the state-to-state approach is developed. Different models for the collision diameters of atoms in excited states are discussed, and it is shown that the Slater-like models can be applied for the state-resolved transport coefficient calculations. The influence of collision diameters of $N$ and $O$ atoms with electronic degrees of freedom on the transport properties is evaluated. Different distributions on the electronic energy are considered for the calculation of transport coefficients. For the Boltzmann-like distributions at temperatures greater than 15000 K, an important effect of electronic excitation on the thermal conductivity and viscosity coefficients is found; the coefficients decrease significantly when many electronic states are taken into account. It is shown that under hypersonic reentry conditions the impact of collision diameters on the transport properties is not really important since the populations of high levels behind the shock waves are low.

## INTRODUCTION

During the last decade electronic degrees of freedom have received a lot attention in the transport kinetic theory [1, 2, 3, 4, 5]. It was shown that in high-temperature flows, neglecting electronic excitation may lead to underestimation in the convective heat flux. The objective of the present study is to generalize our previous one-temperature models of high-temperature reacting flows with electronic excitation [4, 6, 7] including state-to-state kinetics of electronic levels and state-dependent transport coefficients. While the state-to-state model has been widely used in simulations of vibrationally excited flows (see references in [8, 5]), its implementation for gases with electronic excitation is just starting [9, 10, 5, 11].

In the present paper a detailed state-to-state model for a non-equilibrium high-temperature flow of atomic nitrogen $N$ and oxygen $O$ taking into account respectively 170 and 204 electronic energy levels is developed. At this step, ionization is not included since our objective is to study the pure effect of electronic excitation on the transport properties in the state-to-state approach. Our approach makes it possible to evaluate transport terms directly, with no separation of low-lying and high-lying electronically excited states [12, 13, 5]. The transport model is developed on the basis of the modified Chapman-Enskog method [8] and applied to study the transport coefficients under conditions of the spacecraft re-entry (Fire II experiments [14]). The state-to-state distributions are obtained using the results of [12, 13]. The contribution of electronic degrees of freedom into transport coefficients, depending on different collision diameters of excited states, is evaluated.

## MACROSCOPIC PARAMETERS AND GOVERNING EQUATIONS

We consider non-equilibrium flows of atomic gases for which the following relation between characteristic times holds: $\tau_{tr} \ll \tau_{ET} \sim \theta$, here $\tau_{tr}$ and $\tau_{ET}$ are the characteristic times for translational relaxation and electronic energy relaxation, and $\theta$ is the mean time of the variation of gas-dynamic parameters. Under such assumption, relaxation of electronic energy proceeds at the macroscopic time scale and the state-to-state modeling of kinetics and transport

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properties is required. The governing equations take the following form:

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c, \; c = 1, ..., L, \tag{1}$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \boldsymbol{P} = 0, \tag{2}$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \boldsymbol{P} : \nabla \mathbf{v} = 0, \tag{3}$$

here $n_c$ is the number density of atoms on the electronic level $c$ with energy $\varepsilon_c$, $\mathbf{v}$ is the gas velocity, $L$ is the number of accounted levels, $U$ is the total specific energy including electronic one, $\rho U = \frac{3}{2} nkT + \sum_c \varepsilon_c n_c$, $\mathbf{V}_c$ is the diffusion velocity of electronic states, $R_c$ is the production term due to electronic energy transitions, $\rho$ is the mixture density, $\boldsymbol{P}$ is the pressure tensor, $\mathbf{q}$ is the heat flux. This set includes equations (1) of detailed electronic state kinetics. While such an approach is widely used for modeling vibrational relaxation, it is quite novel for electronically excited gases.

Using the procedure of the modified Chapman–Enskog method we derive the expressions for the pressure tensor, diffusion velocity, and heat flux in a viscous flow taking into account state-resolved transport coefficients:

$$\boldsymbol{P} = p\boldsymbol{I} - 2\eta \boldsymbol{S}, \quad \mathbf{V}_c = -\sum_d D_{cd} \mathbf{d}_c - D_{Tc} \nabla \ln T, \quad \mathbf{q} = -\lambda \nabla T - p \sum_c D_{T_c} \mathbf{d}_c + \sum_c \left( \frac{5}{2} kT + \varepsilon_c \right) n_c \mathbf{V}_c. \tag{4}$$

Here $\boldsymbol{S}$, $\boldsymbol{I}$ are deformation rate and unit tensors, $\mathbf{d}_c$ is the diffusive driving force for each electronic state, $p$, $T$ are the pressure and temperature. In the above equations, $\eta$ is the shear viscosity coefficient, $D_{cd}$, $D_{Tc}$ are the diffusion and thermal diffusion coefficients for different electronic states, $\lambda$ is the thermal conductivity coefficient. Note that contrarily to the one-temperature model, in the present case normal mean stress does not include bulk viscosity and relaxation pressure. On the other hand, the thermal conductivity coefficient is specified only by translational degrees of freedom. The transport of electronic energy is governed by the diffusion process. It is worth mentioning that in the one-temperature model for pure atomic gas, thermal diffusion and mass diffusion are absent, and $D_{cd} = D_{Tc} = 0$.

## TRANSPORT COEFFICIENTS

The transport coefficients are derived using the Chapman–Enskog procedure which allows reducing integral equations for the first-order distribution function to the systems of linear algebraic equations using expansions of unknown functions into the series of Sonine polynomials. The expressions for the transport coefficients in terms of the expansion coefficients $b_{c,r}$, $a_{c,r}$, $d^d_{c,r}$ are

$$\eta = \frac{kT}{2} \sum_c \frac{n_c}{n} \, b_{c,0}, \qquad \lambda = \sum_c \frac{5}{4} \, k \, \frac{n_c}{n} \, a_{c,1}, \qquad D_{Tc} = -\frac{1}{2n} \, a_{c,0}, \qquad D_{cd} = \frac{1}{2n} \, d^d_{c,0}. \tag{5}$$

The transport linear systems for the expansion coefficients are derived similarly to [8]. Thus, for the shear viscosity coefficient it is necessary to find the first coefficient $b_{c,0}$ of the system

$$\sum_d H^{cd}_{00} b_{d,0} = \frac{2}{kT} \frac{n_c}{n}, \quad c = 1, ..., L, \tag{6}$$

$H^{cd}_{00}$ is the bracket integral specified by the cross sections of elastic collisions [8].

Thermal conductivity and thermal diffusion are found from the system for the coefficients $a_{c,r}$ supplemented by the constraint required to obtain the unique solution:

$$\sum_d \sum_{r'} \Lambda^{cd}_{rr'} a_{d,r'} = \frac{15kT}{2} \frac{n_c}{n} \delta_{r1}, \; c = 1...L, \quad r = 0, 1, ..., \tag{7}$$

$$\sum_c \frac{\rho_c}{\rho} a_{c,0} = 0, \tag{8}$$



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with $\Lambda_{rr'}^{cd}$ being the corresponding bracket integral. Similarly, for diffusion coefficients we have:

$$\sum_d \Lambda_{00}^{cd} d_{d,0}^b = 3kT\left(\delta_{cb} - \frac{\rho_c}{\rho}\right), \quad b, d = 1, .., L, \tag{9}$$

$$\sum_c \frac{\rho_c}{\rho} d_{c,0}^d = 0, \quad d = 1, .., L. \tag{10}$$

The bracket integrals, after some transformations, can be expressed in terms of collision integrals $\Omega_{cd}^{(l,r)}$ calculated for each pair of excited electronic states, $c$ and $d$. In the present study we calculate the collision integrals using the models proposed in [15] but taking into account increasing diameters of electronically excited atoms.

## SLATER DIAMETER AND EFFECTIVE COLLISION CROSS-SECTION

As indicated in [16], collision integrals for electronically excited states depend significantly on principal quantum number and, consequently, on the collision diameter (i.e. effective cross-section) specified by the atomic radius (i.e. the outermost electron radius). It is worth to note, that no closed analytical form can be given for atomic orbitals of many-electron atoms because the orbital approximation is very primitive [17]. In this case, the actual wave-function can be found using a sophisticated numerical technique which helps to define the so-called Slater-type orbital belonging to a nucleus of an atom of the atomic number $Z$ [17]:

$$\psi(r, \theta, \phi) = Nr^{n^*-1} \exp^{\varsigma r/a_0} Y_{lm_l}(\theta, \phi), \qquad \varsigma = \frac{Z - S}{n^*}, \tag{11}$$

where $N$ is the normalization constant, $n^*$ is the function of effective principal quantum number $n$ (see Table 1), $\varsigma$ is an orbital exponent of a single exponential function, that describes an atomic orbital, $a_0$ is the Bohr radius, $S$ is the screening constant in the Slater orbital [18, 19], $Y_{lm_l}$ is a spherical harmonic, depending on the orbital quantum number $l$ and magnetic quantum number $m_l$. For ground electronic states, the values $Z - S$ have been constructed by fitting Slater-type orbitals to numerically computed wave-functions, see [17]. The latter values now replace those originally proposed by Slater in terms of several simple rules [19].

Using this approach, the collision diameter can be represented via a semi-empirical relation [16]:

$$\sigma_{Slater} = 2r_0 + 1.8\text{Å}, \qquad r_0 = \frac{2n^* + 1}{2\varsigma} a_0, \tag{12}$$

where $r_0$ is the mean electron radius, and the screening constant $S$ for high-lying states should be calculated directly with the set of Slater's rules [19] mentioned above.

For the general quantum number $n$ higher than six, $n > 6$, based on the values for $n^* = 1..6$, we constructed an analytical formula for high-lying electronic states: $n_{h-l}^* = 1.8886 \log n + 0.9124$, that yields the coefficient of determination close to one: $R^2 = 0.9877$.

**TABLE 1.** Quantum number $n$, effective quantum number $n^*$ and data of analytical formula for effective quantum number of high-lying excited stated $n_{h-l}^*$.

| $n$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n^*$ | **1** | **2** | **3** | **3.7** | **4** | **4.2** | - | - | - | - | - | - |
| $n_{h-l}^*$ | 0.91 | 2.22 | 2.99 | 3.53 | 3.95 | 4.30 | **4.59** | **4.84** | **5.06** | **5.26** | **5.44** | **5.61** |

It is worth noting that in the general case, the Slater's formula should be used with care since different orbitals with different values of $n$ but the same values of $l$ and $m_l$ are not orthogonal to one another, and $ns$-orbitals with $n > 1$ have a zero amplitude at the nucleus [17]. In our work we do not account for these exceptions to the basic approximation.

Increasing of the principal quantum number may cause a considerable increase in collision integrals. It was shown, that implementation of the Slater's approach (12) yields over-predicted transport cross section and does not account for the resonant processes of excitation and charge-exchange in collisions involving excited atoms or ion-parent atoms [5, 20]. Nevertheless, at the present time the dependence of collision integrals on the quantum state



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of chemical species is largely unknown and its determination still represents a challenging problem [5]. For excited atoms, collision integrals also depend on polarization of these states and their cross-sections should involve only allowed transitions for electronic energy exchange. Due to the absence of experimental data these effects are not taken into account.

In the modern models [15, 5] of inter-particle potentials, a phenomenological approach is implemented. The phenomenological potentials are constructed combining the well-known Lennard-Jones and Born-Mayer-type potentials which are fitted to experimental results. For such potentials, the collision diameter is a multiplier: $\sigma = x_0 r_e$, where $x_0$ depends on the "softness" of colliding particles and should be found from the potential minimum: $\varphi(x_0) = 0$; and $r_e$ is the parameter depending on the polarizability of colliding particles.

One can mention an attempt [21] to refine the Slater's formula, setting the formulae for each electronic level as a function of $\varsigma$, which depends on $Z$. In the Table 2 collision diameters calculated with the use of different models are presented. In addition to Slater's $\sigma_1$ [19] and Clementi's $\sigma_2$ [21] models, collision diameters for the ground electronic state of atomic nitrogen $N$ and oxygen $O$ are calculated using the Slater's formula with Clementi's data $\sigma_3$ for an orbital exponent $\varsigma$ as well as with data reported by Bruno et al. $\sigma_4$ [15]. It is seen that $\sigma_2$ exceed the remaining ones up to 12 % for $N$ and 23.7 % for $O$ (compared to the most reliable results $\sigma_4$). On the other hand, the discrepancy between $\sigma_1$ and $\sigma_3$ with respect to $\sigma_4$ is small: errors do not exceed 0.3 % and 1 % for $N$, and 1.6 % and 0.8 % for $O$, correspondingly. Therefore we conclude that it is reasonable to use the simple Slater's approach while evaluating the effect of collision diameters on the transport coefficients.

**TABLE 2.** Collision diameters of atomic nitrogen and oxygen at the ground state calculated with different models.

| Atom | Configuration (term) | $\sigma_1$, [Å] | $\sigma_2$, [Å] | $\sigma_3$, [Å] | $\sigma_4$, [Å] |
|---|---|---|---|---|---|
| $N$ | 2s2.2p3(4S) | 3.15686 | 3.52129 | 3.18022 | 3.14663 |
| $O$ | 2s2.2p4(3P) | 2.96303 | 3.72723 | 2.98831 | 3.01248 |

In Table 3, the Slater diameters of the first 1-14 electronic energy levels for $N$ and $O$ are given. It is surprising to see a non-monotonic dependence of diameters on the electronic configuration. Moreover, for the nitrogen states 11-13 we obtain the same collision diameters as for the ground state. For both $N$ and $O$ atoms, the diameters of four low-lying electronic states take the same value as for the ground state.

**TABLE 3.** N and O Atomic Spectra Levels [22, 23] and Slater Diameters Data.

| Electronic level | Configuration (term) | | Electronic level, [cm$^{-1}$] | | $\sigma_{Slater}$, Å | |
|---|---|---|---|---|---|---|
| # | $N$ | $O$ | $N$ | $O$ | $N$ | $O$ |
| 1. | 2s2.2p3 (4S) | 2s2.2p4 (3P) | 0 | 0 | 3.15686 | 2.96303 |
| 2. | 2s2.2p3 (2D) | 2s2.2p4 (3P) | 19224.464 | 158.265 | 3.15686 | 2.96303 |
| 3. | 2s2.2p3 (2D) | 2s2.2p4 (3P) | 19233.177 | 226.977 | 3.15686 | 2.96303 |
| 4. | 2s2.2p3 (2P) | 2s2.2p4 (1D) | 28838.92 | 15867.862 | 3.15686 | 2.96303 |
| 5. | 2s2.2p3 (2P) | 2s2.2p4 (1S) | 28839.306 | 33792.583 | 3.15686 | 2.96303 |
| 6. | 2s2.2p2.3s (4P) | 2s2.2p3.3s (5S) | 83284.07 | 73768.2 | 8.74545 | 8.15013 |
| 7. | 2s2.2p2.3s (4P) | 2s2.2p3.3s (3S) | 83317.83 | 76794.978 | 8.74545 | 8.15013 |
| 8. | 2s2.2p3.3s (4P) | 2s2.2p3.3p (5P) | 83364.62 | 86625.757 | 8.74545 | 8.15013 |
| 9. | 2s2.2p3.3s (2P) | 2s2.2p3.3p (5P) | 86137.35 | 86627.778 | 8.74545 | 8.15013 |
| 10. | 2s2.2p3.3s (2P) | 2s2.2p3.3p (5P) | 86220.51 | 86631.454 | 8.74545 | 8.15013 |
| 11. | 2s2.2p4 (4P) | 2s2.2p3.3p (3P) | 88107.26 | 88630.587 | 3.15686 | 8.15013 |
| 12. | 2s2.2p4 (4P) | 2s2.2p3.3p (3P) | 88151.17 | 88631.146 | 3.15686 | 8.15013 |
| 13. | 2s2.2p4 (4P) | 2s2.2p3.3p (3P) | 88170.57 | 88631.303 | 3.15686 | 8.15013 |
| 14. | 2s2.2p2.3p (2P) | 2s2.2p3.4s (5S) | 93581.55 | 95476.728 | 8.74545 | 18.24683 |

In Fig. 1, Slater diameters as functions of electronic state and electronic energy are presented. For atomic oxygen $O$, the diameter of an excited atom increases faster compared to $N$. For nitrogen electronic levels lower than 25 (with energy less than 12 eV), the diameter is about three times higher than for the ground state. Contrarily to this, for the 14-th level of $O$, $\sigma/\sigma_0$ is about 6, and after some fluctuation in the middle-lying levels 14-50, it shows further increasing. For $N$, the diameter of high-lying states is more stationary: for levels 50-160 the diameter is close to $6\sigma_0$.



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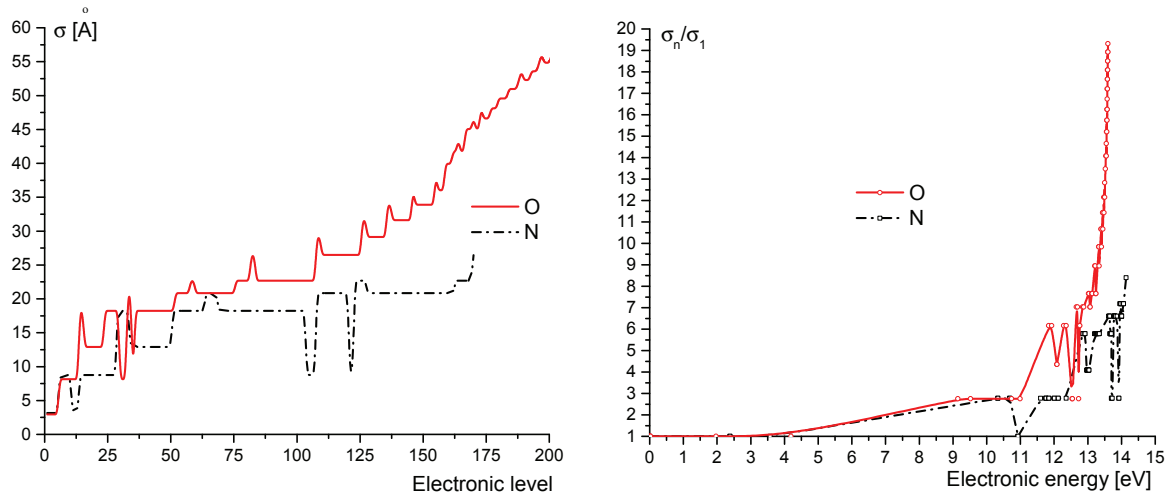


**FIGURE 1.** Slater diameter $\sigma_{Slater}$ as a function of electronic level and electronic energy for *N* and *O*.

## RESULTS AND DISCUSSION

Since rising of principal quantum number leads to a considerable increase in collision integrals, non-equilibrium distributions over excited electronic levels may play an important role in calculation of transport properties. Let us consider the conditions, corresponding to the re-entry of the spacecraft Fire II at the trajectory point 1634 s [14]. The initial conditions before the shock front, $v_0 = 11360$ m/s, $T_0 = 195$ K, $p_0 = 2$ Pa, yield the post-shock temperature $T_1 = 62377$ K and pressure $p_1 = 3827$ Pa. It is obvious that at such a high temperature, the effect of electronic excitation should be taken into account.

The case of Fire II is widely discussed in the literature [12, 13, 24, 25, 6]. In recent works [12, 13], a general mechanism of formation for electronically excited states of atomic species in electron-impact reactions is indicated. It is shown that behind the shock front, within the distance $x = 0 - 1$ cm, the distribution of atomic nitrogen over electronic states becomes non-Boltzmann and represents a combination of the Boltzmann and modified for electronic excitation Saha distributions, while at the distance of about 2.5 cm the distribution is the Boltzmann one or very close to it [12, 13]. Therefore, to study the impact of electronic excitation on the transport properties we consider two kinds of distributions: the combined state-to-state distribution representing a superposition of the Boltzmann and Saha ones taken at the specific point $x = 0.7$ cm ($T = 12000$ K, $p = 4200$ Pa) behind the shock wave [12, 13] (see Fig. 2), and the usual Boltzmann distribution (see Fig. 3) calculated at $x = 2.5$ cm ($T = 9000$ K, $p = 4200$ Pa). Since there is no data on oxygen atom distributions over electronic states, we adopt for *O* the same form of the distribution as for *N*. One can see that at $x = 0.7$ cm, low-lying electronic states are dominating while the population of high-lying states is much lower and tends to the modified Saha distribution. At $x = 2.5$ cm, the distribution is clearly Boltzmannian and high-lying states are widely populated. At the same time, whereas the distribution of low-lying excited states for *N* at $x = 2.5$ cm coincides with the combined one (see Fig. 3), for *O* the population of 1–4 levels is one order of magnitude higher.

Based on the constructed distributions the transport coefficients in the state-to-state approach are calculated taking into account different number of electronic energy levels. In Fig. 4 the thermal conductivity coefficient $\lambda$ of *N* and *O* is shown as a function of $T$ for the combined distribution observed at $x = 0.7$ cm (for fixed $T = 12000$ K), and for the Boltzmann distribution (for different $T$) calculated with 6, 13, 50 and 170 (204) electronic states. While using the combined distribution we take into account all electronic states, 170 for nitrogen and 204 for oxygen. The results are compared with the thermal conductivity coefficient calculated for atomic species at the ground electronic state (solid line); in the latter case the thermal conductivity coefficient coincides with the translational thermal conductivity $\lambda_{tr}$ in the one-temperature approach calculated neglecting the increasing size of excited atoms. Just behind the shock front the distribution over electronic energy is determined mainly by low-lying states, this prevents the thermal conductivity of the sharp decrease. At the same time, the Boltzmann distribution strongly depends on the accounted number of electronic energy levels, and $\lambda$ tends to zero as far as many levels are taken into account. This result is in line with those



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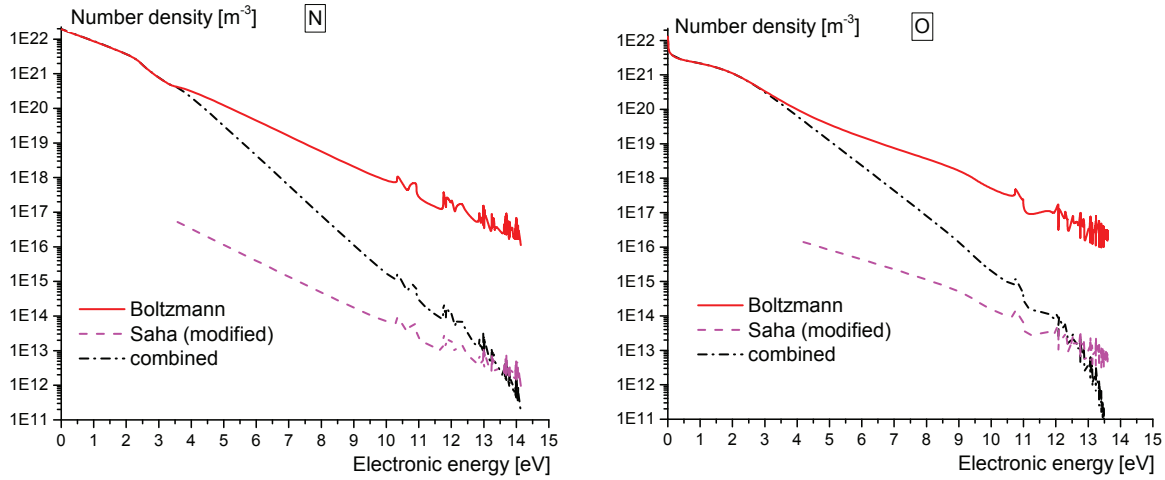


**FIGURE 2.** Population of *N* and *O* electronic energy levels at $x$ = 0.7 cm behind the shock wave for three different distributions.

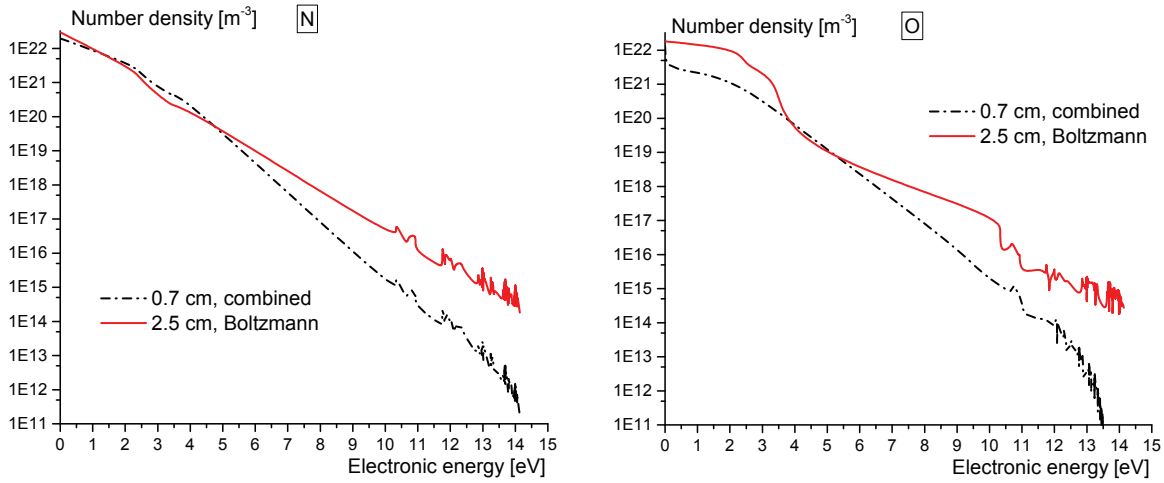


**FIGURE 3.** Population of *N* and *O* electronic energy levels at $x$ = 0.7 cm and 2.5 cm behind the shock wave for two distributions.

reported in [5]. With the rise of principal quantum number for *O* atoms, the collision diameter becomes higher than for *N* (see Fig. 1); this causes a faster decrease of $\lambda$ in oxygen compared to nitrogen. For the combined distribution, thermal conductivity coefficient $\lambda$ nearly coincides with that for the ground electronic state and even becomes a little bit greater for *O*. This is explained by using, for the case of combined distribution, the data of [15] providing the diameter of the ground electronic state about 1.5 % higher than the Slater's one.

In Fig. 5, the shear viscosity coefficient $\eta$ of *N* and *O* as a function of $T$ is given for the same distributions as indicated in Fig. 4. Similarly to $\lambda$, just behind the shock front the distribution over electronic states shows no influence on $\eta$ values, whereas $\eta$ calculated using the Boltzmann distribution strongly depends on the accounted number of electronic energy levels.

Concluding these results it is worth noting, that in the temperature range 1000–14000 K, the state-to-state distributions on the electronic levels do not influence the transport coefficients. On the other hand, in the beginning of the relaxation zone where the temperature is quite high (14000–60000 K), the populations of high-lying electronic states are low, which also makes it possible to neglect them in calculations of the transport terms.



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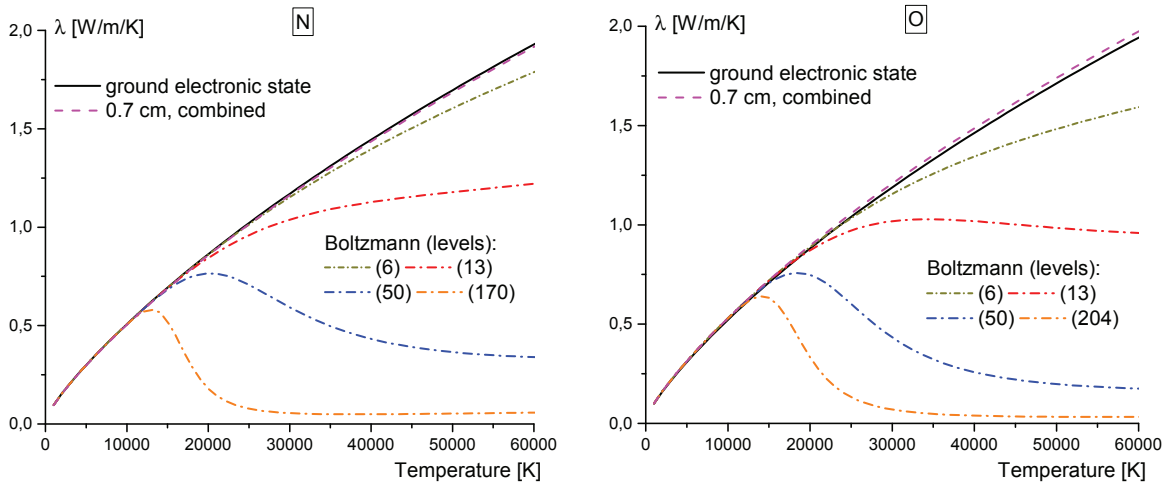


**FIGURE 4.** Thermal conductivity $\lambda$ of $N$ and $O$ as a function of $T$ for three cases: 1) the ground electronic state; 2) the combined distribution ($x$ = 0.7 cm, $T$ = 12000 K); and 3) the Boltzmann distribution taken for different number of electronic energy levels.

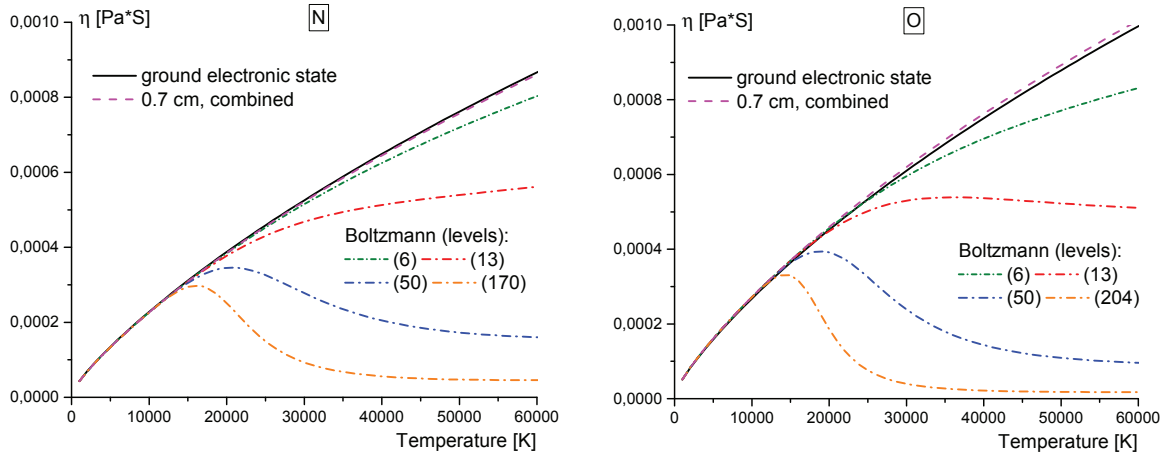


**FIGURE 5.** Shear viscosity $\eta$ of $N$ and $O$ as a function of $T$ for three cases: 1) the ground electronic state; 2) the combined distribution ($x$ = 0.7 cm, $T$ = 12000 K); and 3) the Boltzmann distribution taken for different number of electronic energy levels.

## CONCLUSION

A theoretical model for the state-specific transport coefficients in atomic gases with electronically excited states is developed. The influence of greatly increasing collision diameters on the transport properties of high-temperature $N$ and $O$ atoms is evaluated. In particular, it is confirmed that the Slater-like models can be used for preliminary estimates of the state-resolved transport coefficients. A non-monotonic dependence of collision diameters for low-lying states of $N$ and $O$ on the electronic energy is indicated. It is shown that for atomic oxygen $O$, the diameter of an excited atom increases faster than for $N$, which affects the transport coefficients of $O$. Different distributions on electronic energy levels are taken into account while simulating the thermal conductivity and viscosity coefficients. In the temperature range 1000–14000 K the transport coefficients calculated using the state-to-state and one-temperature models and different number of excited levels take practically the same values. On the contrary for higher temperatures, increasing collision diameters of excited atoms cause a strong decrease in the transport coefficients calculated on the basis of the Boltzmann distributions, especially for the case when all electronic states are considered. This interesting effect does not however affect the flow around reentering vehicles since in the high-temperature region just behind the bow shock,



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the populations of high levels do not follow the Boltzmann distribution, and molar fractions of high-lying states are quite low. This encouraging conclusion justifies implementation of simplified transport models for hypersonic flow simulations. However in other plasma applications, when highly located electronic states are significantly populated, the state-specific transport coefficients may considerably modify the predicted heat and mass transfer.

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## REFERENCES

[1] D. Bruno, A. Laricchiuta, M. Capitelli, and C. Catalfamo, Phys. Plasmas **14**, p. 022303 (2007).
[2] E. Kustova and L. Puzyreva, Phys. Rev. E **80**, p. 046407 (2009).
[3] V. Istomin, E. Kustova, and L. Puzyreva, "Transport properties of electronically excited $N_2$/N and $O_2$/O mixtures," in *Rarefied Gas Dynamics*, AIP Conference Proceedings, Vol. 1333, edited by D. Levin et al. (American Institute of Physics, Melville, NY, 2011), pp. 667–672.
[4] V. Istomin and E. Kustova, "Transport properties of five-component nitrogen and oxygen ionized mixtures with electronic excitation," in *Rarefied Gas Dynamics*, AIP Conference Proceedings, Vol. 1501, edited by M. Mareschal and A. Santos (American Institute of Physics, Melville, NY, 2012), pp. 168–174.
[5] M. Capitelli, D. Bruno, and A. Laricchiuta, *Fundamental Aspects of Plasma Chemical Physics: Transport*, Springer Series on Atomic, Optical, and Plasma Physics, Vol. 74 (Springer Verlag, Berlin, 2013).
[6] V. Istomin and E. Kustova, "Effect of electronic excitation on high-temperature flows behind strong shock waves," in *Rarefied Gas Dynamics*, AIP Conference Proceedings, Vol. 1628, edited by J. Fan (American Institute of Physics, Melville, NY, 2014), pp. 1221–1228.
[7] V. A. Istomin, E. V. Kustova, and M. A. Mekhonoshina, J. Chem. Phys. **140**, p. 184311 (2014).
[8] E. Nagnibeda and E. Kustova, *Nonequilibrium Reacting Gas Flows. Kinetic Theory of Transport and Relaxation Processes* (Springer-Verlag, Berlin, Heidelberg, 2009).
[9] A. Aliat, A. Chikhaoui, and E. Kustova, Phys. Review E **68**, p. 056306 (2003).
[10] A.Aliat, E. Kustova, and A. Chikhaoui, Chem. Phys. **314**, 37–47 (2005).
[11] A. Guy, A. Bourdon, and M.-Y. Perrin, Physics of Plasmas **22**, p. 043507 (2015).
[12] C. O. Johnston, *Nonequilibrium shock-layer radiative heating for Earth and Titan entry* (Virginia Polytechnic Institute and State University, Virginia, USA, 2006).
[13] T. E. Magin, M. Panesi, A. Bourdon, and A. Bultel, Center for Turbulence Research Annual Research Briefs, Aeronautics and Aerospace Department, von Karman Institute for Fluid Dynamics, Belgium 159–171 (2008).
[14] D. L. Cauchon, "Radiative heating results from fire ii flight experiment at a re-entry velocity of 11.4 km/s," Tech. Rep. X-1402 (NASA, NASA Technical Memorandum).
[15] D. Bruno, M. Capitelli, C. Catalfamo, R. Celiberto, G. Colonna, P. Diomede, D. Giordano, C. Gorse, A. Laricchiuta, S. Longo, D. Pagano, and F. Pirani, "Transport properties of high-temperature mars-atmosphere components," ESA STR 256 (ESA, Noordwijk: ESA Publications Division, 2008).
[16] J. Hirschfelder, J. Chem. Phys. **26**, 282–285 (1957).
[17] P. Atkins and R. Friedman, eds., *Molecular Quantun Mechanics*, 4th ed. (Oxford University Press, 2005).
[18] C. Zener, Phys. Rev. **36**, 51–56 (1930).
[19] J. C. Slater, Phys. Rev. **36**, 57–64 (1930).
[20] V. Istomin, E. Kustova, and M. Mekhonoshina, "Validity of eucken formula and stokes viscosity relation in high-temperature electronically excited gases," in *Rarefied Gas Dynamics*, AIP Conference Proceedings, Vol. 1628, edited by J. Fan (American Institute of Physics, Melville, NY, 2014), pp. 1229–1236.
[21] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686–2689 (1963).
[22] J. R. A. Kramida, Yu. Ralchenko and N. A. Team, *NIST Atomic Spectra Database (ver. 5.3), [Online]* (National Institute of Standards and Technology, Gaithersburg, MD, 2015).
[23] C. E. Moore, *Tables of Spectra of Hydrogen, Carbon, Nitrogen, and Oxygen Atoms and Ions, in CRC Series in Evaluated Data in Atomic Physics* (CRC Press, Boca Raton, FL, 1993).
[24] M. Panesi, T. E. Magin, A. Bourdon, A. Bultel, and O. Chazot, J. Thermophys. Heat Transfer **23**, 236–248 (2009).
[25] M. Panesi, *Physical models for nonequilibrium plasma flow simulations at high speed re-entry conditions* (von Karman Institute, Rhode-Saint-Genese, Belgium, 2009).



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